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Photocatalytic, photolytic and radiolytic elimination of imidacloprid from aqueous solution: reaction mechanism, efficiency and economic considerations

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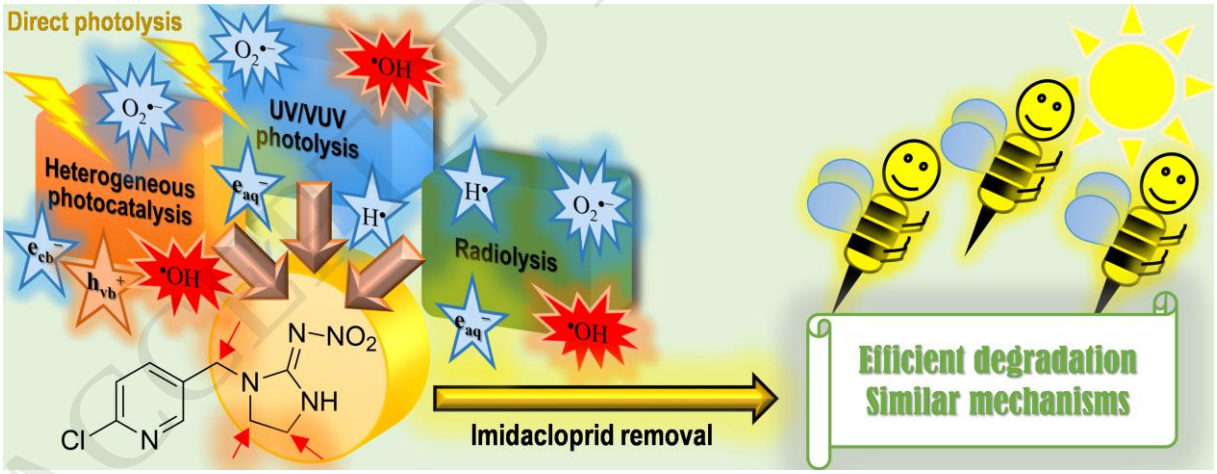
Graphical Abstract



Highlights

- In heterogeneous photocatalysis anaerobic degradation of imidacloprid occurred

- Independently of the method the same products form at the beginning of the treatment
- Alpha-aminoalkyl radicals play a key role in degradation
- •OH attacks the heterocyclic ring and the CH_2 bridge between the two rings
- In photocatalytic degradation of imidacloprid charge transfer plays important role
- Photocatalysis, UV/VUV and radiolysis are recommended for practical application

Abstract: The purpose of this work was the comparison of imidacloprid transformation in heterogeneous photocatalysis (TiO_2), $UV_{254\ nm}$ photolysis, $UV_{254\ nm}/VUV_{185\ nm}$ photolysis and γ-radiolysis (also pulse radiolysis) in the presence and absence of dissolved oxygen, and the identification of intermediates formed during the applied treatments. All the methods tested were effective in the degradation of imidacloprid in 10^{-4} mol dm^{-3} aqueous solution. In most cases the mineralization (TOC) and the disappearance of the starting molecules (detected by HPLC/DAD) occurs parallel. However, when the starting molecules were eliminated in oxygenated solutions the highest decrease in TOC values were only 30-40% in UV/VUV and TiO_2/O_2 systems. In radiolysis and UV photolytic systems these values were 10-15%. In the absence of oxygen the mineralization was usually slower than in its presence. Beside the dominant photocatalytic process, a small-scale contribution of direct photolysis was observed in TiO_2 containing suspensions, irradiated with 300-400 nm light.

Hydroxyl radicals show low reactivity with the N-containing aromatic ring, they attack the heterocyclic 5-member ring and the CH_2 bridge between the two rings in direct oxidation or in H-abstraction. In these reactions carbon centred α-aminoalkyl radicals form. In the presence of dissolved oxygen these radicals transform to hydroxylated or carbonylated stable products. Scavenging experiments suggest that in TiO_2 photocatalytic degradation beside hydroxyl radical based transformation, direct charge transfer has also important role in the degradation. Based on the degradation and mineralization results with imidaloprid, photocatalysis, UV/VUV photolysis and radiolysis are recommended for practical application, economic considerations (E_{EO}) suggest radiolysis as the method requiring lowest electric energy consumption.

Keywords

Degradation, radical mechanism, direct photolysis, charge transfer, intermediates

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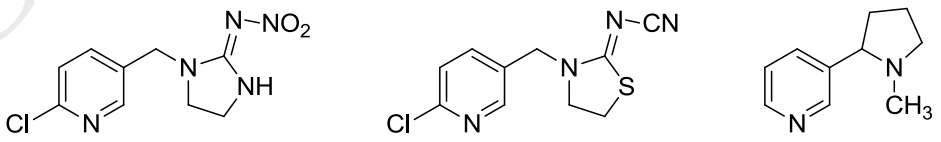
1. Introduction

Imidacloprid (*N*-{1-[(6-Chloro-3-pyridyl)methyl]-4,5-dihydroimidazol-2-yl}nitramide, Fig. 1) belongs to the class of neonicotinoid insecticides which act on the central nervous system of insects. Neonicotinoids are extensively used in agriculture for e.g., sunflower, corn, cotton, potato, sugar beets, rice, soy, rapeseed, fruits and ornamental plants [1] to keep away numerous sucking and biting pest insects, including aphides, some lepidoptera, whiteflies and beetles.

Imidacloprid is the first neonicotinoid produced since 1994. Nowadays, it is one of the most used pesticides in the world. This pesticide was found to have high toxicity to beneficial insects, such as the honeybee, insectivorous birds, animals living in the lakes and rivers [2,3]. A high fraction of the pesticides applied in the fields ends up in surface waters. Imidacloprid poses particular threat to the environment due to its extensive use, relatively high solubility (0.58 g dm^{-3}) and high persistence in surface waters. Advanced oxidation processes (AOP) are recommended for the elimination of the recalcitrant organic molecules from aqueous solutions. Although, there are several publications on the degradation of imidacloprid, usually only one AOP technique is used (e.g., heterogeneous photocatalysis, UV or UV/VUV photolysis) and direct comparison is barely made.



Imidacloprid Thiacloprid Nicotine

Figure 1. The structure of imidacloprid, thiacloprid and nicotine.

In heterogeneous photocatalysis, a semiconductor metal oxide (in most cases TiO_2) is exposed to UV-visible light. When the energy of the absorbed photon is higher than the band gap energy, the photon absorption results in the excitation of an electron from the valence band to the conduction band (e_{cb}^-), and a hole (h_{vb}^+) is created (Eq. (**1**)) [4]. In the absence of effective electron scavenger h_{vb}^+ and e_{cb}^- undergo fast recombination. When dissolved oxygen (DO) is present, it serves as an effective electron scavenger. If h_{vb}^+ and e_{cb}^- escape recombination, after travelling to the surface, e_{cb}^- can transform to superoxide radical anion ($O_2^{\bullet -}$) and h_{vb}^+ to hydroxyl radical ($^\bullet$OH) (Eqs. (**2-6**)). In photocatalysis, adsorption on the surface of the catalyst has a crucial role. The transformation of organic substances (OS) can take place *via* direct charge transfer and/or *via* reaction with $^\bullet$OH on the surface ($^\bullet OH_{surf}$) or in the bulk ($^\bullet OH_{bulk}$) (Eqs. (**7-9**)). The contribution of these pathways to the transformation of target organic substances depends not only on the properties of the photocatalyst and the model compound, but also on the experimental conditions [5,6,7,8,9].

$TiO_2 + h\nu\ (\lambda < 410\ nm) \rightarrow e^- + h^+ \rightarrow e_{cb}^- + h_{vb}^+$ (**1**)

$h_{vb}^+ + {}^-OH\ (H_2O) \rightarrow {}^\bullet OH_{surf}\ ({}^\bullet OH_{surf} + H^+) \rightarrow {}^\bullet OH_{bulk}\ (+ H^+)$ (**2**)

$e_{cb}^- + O_2 \rightarrow O_2^{\bullet -}$ (**3**)

$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet$ (**4**)

$O_2^{\bullet -} + HO_2^\bullet + H_2O \rightarrow H_2O_2 + O_2 + {}^-OH$ (**5**)

$e_{cb}^- + H_2O_2 \rightarrow {}^\bullet OH_{surf} + OH^-$ (**6**)

$OS + h^+$ (**7**)

$OS + {}^\bullet OH_{surf}$ $\rightarrow$ oxidized products (**8**)

$OS + {}^\bullet OH_{bulk}$ (**9**)

Using immobilized TiO_2 for solar photolysis in a demonstration equipment, Malato *et al.* [6] showed that the same imidacloprid transformation products form during TiO_2 photocatalysis and during photo Fenton reactions. $^\bullet$OH mainly attacks the 4,5-dihydroimidazol-2-yl-nitramide part of the molecule, e.g., replacing =N-NO_2 by =O. The main stable products were found to be 2-pyrrolidone and chloronicotinic acid. Dechlorination has a low probability [6,8]. The 254 nm photons of a low-pressure mercury vapour lamp (LP) with commercial quartz window are directly absorbed by the imidacloprid molecules (Fig. 2) [10,11,12]. Using high-pressure mercury lamp ($\lambda > 280$ nm) for the irradiation of aqueous solutions, Wamhoff and Schneider [13] reported 1-[(6-chloro-3-pyridinyl)methyl]-2-imidazolidinone as the main degradation product. In the latter work and in other publications several isomers of products having two carbonyl groups were also reported [8,13,14].

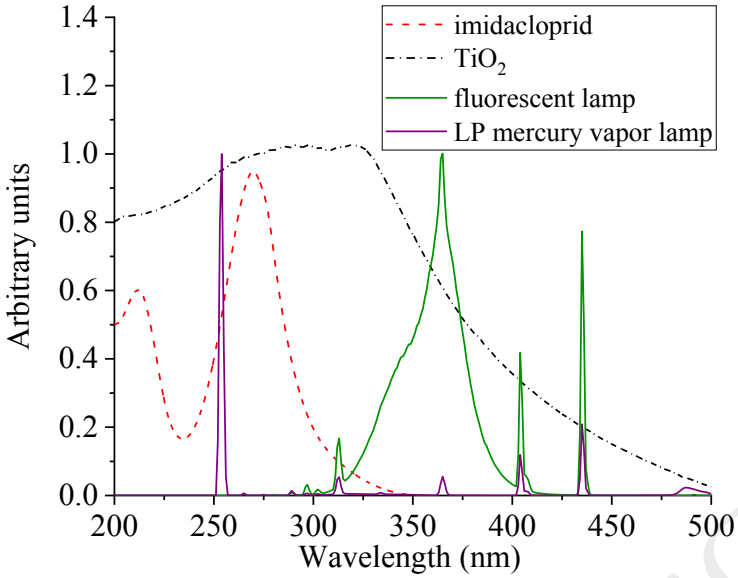


Figure 2. Emission spectra of the UV (LP mercury vapor) and fluorescent lamps and the absorption spectra of imidacloprid and TiO_2.

When the LP lamp is equipped with high purity silica window, the 185 nm VUV photons also reach the sample of interest. The 185 nm photons excite the water molecules, and the formed hydrogen atom ($H^{\bullet}$) and $^{\bullet}OH$ intermediates also react with the solute molecules. The quantum yield of water decomposition at 185 nm is 0.33. At this wavelength the photons are absorbed within a few millimetres, so the reaction zone is rather narrow [15]. With very low quantum yield ($\phi < 0.05$) hydrated electrons (e_{aq}^-) are also generated.

In radiolysis of dilute solutions the decomposition of water molecules gives $^{\bullet}OH$, e_{aq}^- and $H^{\bullet}$, as primary species, with yields (*G*-values) of 0.280, 0.280 and 0.062 μmol J^{-1}, respectively [16,17]. *G*-value is the basic unit in radiation chemistry defined as the moles of a specified entity, produced, destroyed or changed by radiation upon absorption of 1 Joule of energy by the matter. Unlike VUV photolysis, γ- or pulse radiolysis results in a homogenous system and e_{aq}^- may have a significant role in the transformation of target substances.

The radiolytic degradation of imidacloprid was investigated e.g., by Ramírez *et al.* [18]. Using various dissolved gases the radical composition formed in solutions can be modified. In the presence of DO, the $H^{\bullet}/e_{aq}^-$ reductive primary species transform to less reactive $HO_2^{\bullet}/O_2^{\bullet-}$ pair (pK_a 4.8) (Eqs. (**10**) and (**11**)).

$H^{\bullet} + O_2 \rightarrow HO_2^{\bullet}$ $\quad k = 1.2 \times 10^{10}$ mol^{-1} dm^3 s^{-1} **(10)**

$e_{aq}^- + O_2 \rightarrow O_2^{\bullet-}$ $\quad k = 1.9 \times 10^{10}$ mol^{-1} dm^3 s^{-1} **(11)**

Consequently, in O_2 containing solutions the main reaction partner of the organic pollutants in both VUV- and γ-irradiation is $^{\bullet}OH$, but the $O_2^{\bullet-}/HO_2^{\bullet}$ pair may also have some contribution to the transformation of solute molecules [19]. In the radiation chemical practice, the reactions of $^{\bullet}OH$ are generally investigated in N_2O saturated solution [17], in order to transform e_{aq}^- to $^{\bullet}OH$ (Eq. (**12**)). The usual practice in $H^{\bullet}$ reaction investigations is to remove DO with N_2 bubbling and setting the pH to the acidic range to transform e_{aq}^- to $H^{\bullet}$ (Eq. (**13**)). In order to eliminate $^{\bullet}OH$ reaction with the target compound, *t*-butanol is added to the solution (Eq. (**14**)):

$$N_2O + e_{aq}^- + H_2O \rightarrow {}^{\bullet}OH + OH^- + N_2 \quad (\mathbf{12})$$

$$H_3O^+ + e_{aq}^- \rightarrow H_2O + H^{\bullet} \quad (\mathbf{13})$$

$$(CH_3)_3COH + {}^{\bullet}OH \rightarrow {}^{\bullet}CH_2(CH_3)_2COH + H_2O \quad (\mathbf{14})$$

t-Butanol as $^{\bullet}OH$ scavenger and N_2 bubbling is also used in studying e_{aq}^- reactions (pH > 6). The novelty of this work is the comparison of imidacloprid transformation in heterogeneous photocatalysis, $UV_{254\ nm}$ photolysis, $UV_{254\ nm}/VUV_{185\ nm}$ photolysis, γ-radiolysis and pulse radiolysis in the presence and absence of DO, and the identification of intermediates formed during the applied treatments. Such an extensive comparison between imidacloprid degradation methods is missing from the literature, especially comparison of the other methods with gamma radiolysis. The radical composition during these processes differs considerably. Based on these differences we expect to obtain a clearer picture about the processes taking place during photocatalysis. For instance, the different radiolytic techniques give possibilities for separate investigation of $^{\bullet}OH$, e_{aq}^- and $H^{\bullet}$ reactions, and for the direct determination of the rate constants. Thus, they may strongly contribute to clarifying the details of reaction mechanisms. At the same time we investigate the applicability of the techniques in removal of the starting molecules, their products, the total organic content of the liquid and the economical feasibilities.

2. Experimental

2.1. Materials and methods

Sigma-Aldrich and VWR Chemicals provided analytical standard imidacloprid (> 98%). Methanol was purchased from VWR Chemicals (HiPerSolv CHROMANORM, super gradient grade for HPLC) and acetic acid (99-100%) from Molar Chemicals Ltd. Potassium ferricyanide ($K_3[Fe(CN)_6]$), KI, EDTA, NaCl, NaF and chloroform were obtained from Sigma-Aldrich, and *t*-butanol from Spectrum 3D. High purity water was prepared through Milli-Q Integral Water Purification System (MerckMillipore).

Most of the experiments were made in 1.0×10^{-4} mol dm^{-3} aqueous imidacloprid solutions. For the photolytic degradation two light sources have been assembled: one to perform the UV photolysis, the other one for the UV/VUV photolysis. The lamps were fabricated by LightTech and have the same geometry (307 mm long and 20.5 mm external diameter of the sleeve) and electric parameters (15 W electric and 4.0 W UV output). The UV lamp was covered with commercial quartz sleeve and supplied photons at 254 nm (GCL307T5VH/CELL). The UV/VUV lamp emitted also at 185 nm (GCL307T5/CELL) because it was covered with a special Suprasil quartz sleeve. Before turning on the lamp, the solutions had been circulated through the system for 15 min (in the case of O_2) or 30 min (in the case of N_2).

In heterogeneous photocatalytic experiments the TiO_2 (Degussa P25, Evonik Aeroxide) concentration was usually 1.0 g dm^{-3}. Irradiation was performed with a fluorescent UV lamp (GCL303T5/UVA, LighTech, Hungary, dimensions: 307 mm × 20.5 mm, 15 W electric output) emitting in the range of 300−400 nm with λ_{max} = 365 nm (Fig. 2). The photon flux of the light source was 1.2×10^{-5} mol$_{photon}$ s^{-1}, determined by ferrioxalate actinometry [20]. The reactor parameters were the same as those of the UV and UV/VUV reactors. To remove the photocatalyst particles, after irradiation the samples were centrifuged and filtered with syringe filter (Sartorius Stedim, Ministart®-plus, 0.20 μm).

In γ-radiolysis experiments 5 mL ampoules with 1.0×10^{-4} mol dm^{-3} imidacloprid solution were placed at an equal distance from the ^{60}Co-γ source of a panoramic type irradiator, to have a dose rate of 0.7 kGy h^{-1} (700 J kg^{-1} h^{-1}). The solutions were irradiated in open ampoules (air saturated) or in sealed ampoules (in the absence of DO).

Pulse radiolysis investigations were carried out using 800 ns pulses of accelerated electrons, applying 20 Gy/pulse (J kg^{-1}/pulse) [21]. In this technique, fast energy absorption from short pulses of accelerated electrons initiates the degradation of water. Reactive intermediates of water radiolysis form during the pulse and react with the solute molecules on a longer timescale. With the optical detection applied, the time dependence of the absorption of intermediates can be followed.

2.2. Analytical techniques

The UV-Vis spectrophotometric measurements were performed with an Agilent 8453 equipment using a 0.5 cm path-length cuvette. Samples were analyzed by HPLC-DAD system consisting of an Agilent 1100 Series chromatograph coupled with a diode array detector (DAD). The isocratic separation was performed using a reverse-phase C18 column

(LiChroCART 250-4 LiChrospher 100, pore size 5 µm) produced by MerckMillipore. A mixture of methanol and 1% acetic acid aqueous solution (50:50 v/v) was used as eluent. Analysis was conducted according to the following settings: flow rate 1.0 cm^3 min^{-1}, column temperature 25 °C, injection volume 20 µL, pressure 207 bar, detection wavelength 270 nm. Under these conditions, imidacloprid eluted at 3.60 min. The standard deviation of the measured values was less than ±5% in each cases.

The decomposition of imidacloprid was characterized by the initial rate of transformation, obtained from linear regression fits to the pesticide concentration-irradiation time plot, up to 30-35% of the concentration of the transformed target compound.

In the case of heterogeneous photocatalysis, the imidacloprid adsorbed on the TiO_2 surface was measured in the suspension having 1.0 and 1.5 g dm^{-3} TiO_2 dosage. The solution was stirred for 1 hour in dark and samples were taken at 0, 20, 40, 60 min time intervals.

The identification of intermediate products was performed using HPLC-DAD coupled with a mass spectrometer equipped with Electrospray Ionization (ESI) source and a triple quadrupole analyzer (QqQ) (Agilent 1100, LC/MSD VL). Both negative (ESI(-)) and positive (ESI(+)) ionization modes have been used, the fragmentor and the capillary voltages were 90 V and 3000 V, respectively. The mass range was set between 50 and 300 amu.

The mineralization of imidacloprid was followed by Total Organic Carbon (TOC) measurements performed with TOC Analytik Jena Multi N/C 3100-type instrument. Potassium hydrogen phthalate was used for the calibration.

2.3. Energy requirements, Electric Energy per Order (E_{EO})

The applied AOP methods were compared by Electric Energy per Order (E_{EO}) calculations. This calculation enables the economic comparison of the different irradiation techniques. It represents the amount of electric energy required for reduction of the target compound concentration in a unit volume [e.g., 1 m^3] by one order of magnitude [15]. In batch operation E_{EO} values [kWh m^{-3} $order^{-1}$] can be calculated using **Eq. (15)**.

$$E_{EO} = \frac{P \times t \times 1000}{V \times \lg(c_i/c_f)} \qquad \textbf{(15)}$$

where P is the rated power [kW] of the AOP system, V is the volume [dm^{-3}] of water, t is the treatment time [h], c_i and c_f are the initial and final concentrations [mol dm^{-3}], respectively, of the compound investigated. Multiplication by 1000 is due to converting dm^3 to m^3.

3. Results

3.1. Pulse radiolysis experiments

The transient absorption spectrum shown in Fig. 3 was measured in N_2O saturated solution 8 μs after the pulse. In such solution •OH is the main reacting radical. In the spectrum there is a well-resolved strong absorbance at 330 nm and two other bands at ~525 nm and 250 nm. For imidacloprid these spectral characteristics, the places of absorption bands and the intensities are similar to the characteristics of the spectrum of the transient(s) detected in the •OH + thiacloprid reaction [22]. At the same time, both spectra are similar to the spectrum characterizing the •OH + nicotine system published by Kosno *et al.* [23], with λ_{max} at 330 nm and at ~470 nm.

To identify the transient intermediates, the spectrum was measured also in the presence of 10^{-4} mol dm^{-3} ferricyanide ions. These ions are known to react with radicals that can be easily oxidized. Strong decrease in the absorbances at 330 nm and at 525 nm indicates the formation of such radical species in the system. Ferricyanide ions eliminate the hydroxycyclohexadienyl (HCH) radical isomers that may form in •OH addition to the aromatic ring, transforming them to phenol type molecules [22]. HCH radicals formed from aromatic molecules have wide absorption bands with maxima between 300-400 nm and molar absorbances of 3000-6000 mol^{-1} dm^3 cm^{-1}. Assuming that all of the •OH radicals react with imidacloprid producing HCH radicals, a molar absorbance of ~2000 mol^{-1} dm^3 cm^{-1} was calculated at 330 nm.

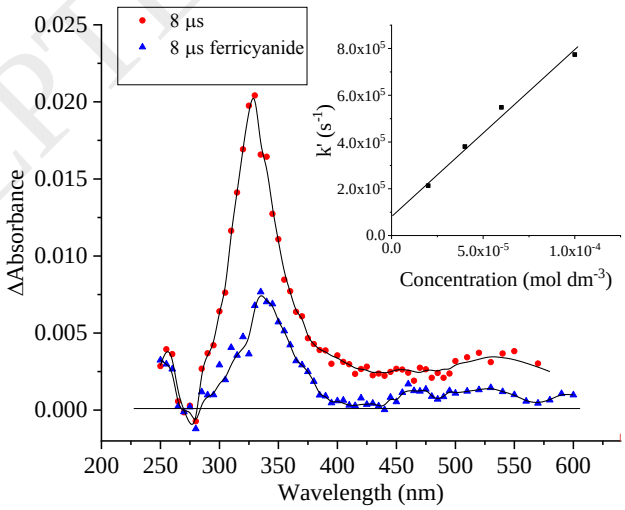


Figure 3. Transient absorption spectra measured in 10^{-4} mol dm^{-3}, N_2O saturated imidacloprid solution (by pulse radiolysis with optical detection), 8 μs after the pulse, without and with 10^{-}

^{4} mol dm^{-3} ferricyanide. Inset: concentration dependence of the pseudo-first-order rate constant (k') of absorbance build-up at the absorbance maximum (330 nm).

Beside HCH radicals ferricyanide ions may also react with several other radical species, including benzyl radicals and α-aminoalkyl radicals (Fig. 4, 2-4) [22]. These radicals can form in the $^{\bullet}$OH + imidacloprid reaction by hydrogen atom elimination from the CH_2 units. H elimination from the bridge between the two rings (Fig. 4, 2) is highly favoured due to resonance stabilization of the unpaired electron by the aromatic ring (benzyl type radical) and by the imidazolidine ring (α-aminoalkyl radical). At the same time, α-aminoalkyl radicals may also form by H-abstraction from the CH_2 units in the 5-member ring (Fig. 4, 3-4). Dell'Arciprete *et al.* [24,25] used $SO_4^{\bullet-}$ and $CO_3^{\bullet-}$ radical anions for imidacloprid (and two other neonicotinoids) oxidation, while Kosno *et al.* [23] oxidized nicotine by $N_3^{\bullet}$ radicals. These radicals pick up an electron from one of the ring N-atoms, followed by a deprotonation step yielding α-aminoalkyl radical. The obtained absorption spectra are similar to the spectrum detected here for the $^{\bullet}$OH + imidacloprid reaction, strongly suggesting the participation of α-aminoalkyl radicals in $^{\bullet}$OH induced degradation.

The spectra of intermediates may belong either to HCH radicals or to α-aminoalkyl type radicals. There are several evidences contradicting the idea that HCH radicals playing important role in imidacloprid degradation.

1. $^{\bullet}$OH reacts faster with imidacloprid as expected for radical addition to the aromatic ring. The rate constant of the $^{\bullet}$OH + imidacloprid reaction was determined by measuring the pseudo-first-order rate constants of absorbance build-up at the 330 nm maximum at several imidacloprid concentrations. The slope of the pseudo-first-order rate constant – imidacloprid concentration plot (Fig. 3, Inset) supplied a second order rate constant of $(6.97\pm0.54) \times 10^9$ mol^{-1} dm^3 s^{-1}. This rate constant is higher than that measured for thiacloprid (4.8×10^9 mol^{-1} dm^3 s^{-1} [22]) in the same laboratory with the same technique, but it agrees with the value determined for nicotine (6.7×10^9 mol^{-1} dm^3 s^{-1} [23]) using also pulse radiolysis technique. Our value for imidacloprid is much higher than that published by Turabik *et al.* [26] using the less reliable competitive technique: 1.23×10^9 mol^{-1} dm^3 s^{-1}. As reference compound they used 4-hydroxybenzoic acid with $k_{\bullet OH}$ of 2.19×10^9 mol^{-1} dm^3 s^{-1}. However, this reference value (determined also in competitive experiments) is too low. If we use 7×10^9 mol^{-1} dm^3 s^{-1} [27] for the reference value (determined in pulse radiolysis) a more realistic, $\sim 4 \times 10^9$ mol^{-1}

$dm^3\ s^{-1}$ rate constant is obtained. Dell'Arciprete *et al.* [28] determined 5.5×10^{10} $mol^{-1}\ dm^3\ s^{-1}$ for the rate constant. This value is unrealistic, since it is half of an order of magnitude higher than the theoretical maximum, the diffusion controlled rate constant (1.1×10^{10} $mol^{-1}\ dm^3\ s^{-1}$, [29]). Dell' Arciprete *et al.* [28] determined the rate constant by the SCN^- competition technique which often gives false results (see e.g., [23,30]).

In aqueous pyridine solution, when •OH reacts with the solute in radical addition, in the first step HCH radicals form with a rate constant of 3×10^9 $mol^{-1}\ dm^3\ s^{-1}$ [31]. The rate constant of reaction with the pyridine ring in imidacloprid is expected to be smaller due to the deactivating effect of the chlorine atom on the ring. In the reaction several HCH radical isomers may form, Fig. 4 by number 1 shows one of them. For 2-chloropyridine a rate constant of 1.8×10^9 $mol^{-1}\ dm^3\ s^{-1}$ has been reported [32].

2. In reactions of the HCH radicals, aromatic molecules with OH substituent are expected as stable products. Such stable products were not observed in this work, and their formation is not mentioned in the literature. However, oxidations of the CH_2 groups in the molecules to CH-OH or C=O are reported in several publications [28].

3. In the reactions of •H with the aromatic rings usually cyclohexadienyl radicals (CH) form. The spectra of these CH radicals are practically identical with that of the HCH radicals since the OH on the ring is not part of the conjugated electron system. In •H reaction with imidacloprid no spectral peak was observed at 330 nm (spectrum is not shown), indicating that the 330 nm absorbance formed in the reaction of •OH is basically not due to the HCH radicals. Based on the build-up of a signal at about 300 nm a rate constant of 2.22×10^9 $mol^{-1}\ dm^3\ s^{-1}$ was calculated for the •H reaction.

We may conclude that •OH primarily attacks the heterocyclic ring and the CH_2 bridge between the two rings in reactions yielding α-aminoalkyl radicals (Fig. 4, 2-4).

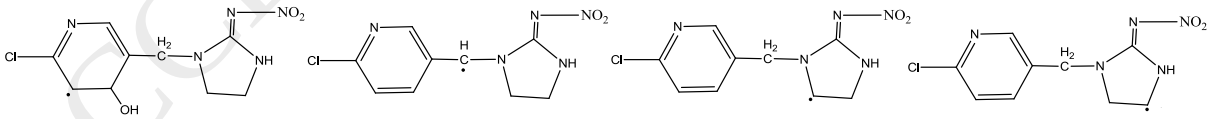


Figure 4. Radicals expected to form in •OH + imidacloprid reaction.

Several experiments were also conducted to study the reactions of e_{aq}^- in deoxygenated solutions containing *t*-butanol to remove •OH (Eq. (**14**)). Imidacloprid was found to react with e_{aq}^- with a relatively high rate constant of 5.1×10^9 $mol^{-1}\ dm^3\ s^{-1}$. The e_{aq}^- adduct spectrum was very weak and characterless (not shown).

3.2. Decomposition during heterogeneous photocatalysis

3.2.1. Degradation in TiO_2 photocatalysis

Since reactions can take place on the surface or close to the surface of photocatalyst, the extent of adsorption has to be studied. Suspending 1.0 g dm^{-3} TiO_2 into 1.0×10^{-4} mol dm^{-3} imidacloprid solution caused no measurable concentration change due to the adsorption of imidacloprid on the catalyst surface, even at higher photocatalyst concentrations (1.5 g dm^{-3}) indicating low absorption capacity. However, the degradation results, detailed below, suggest reactions at the surface. It should be mentioned, that Ahmari *et al.* [9] reported some imidacloprid adsorption on TiO_2 nanoparticles.

The optimal photocatalyst concentration was determined in both oxygen-free and DO containing suspensions. In DO containing solution with increasing TiO_2 concentration; fast increase in transformation rate was observed up to 0.5 mg dm^{-3} (Fig. 5). This increase is due to the higher surface area of photocatalyst (irradiated with UV light) available for photocatalytic reaction. Above 0.5 mg dm^{-3} TiO_2 concentration, saturation is observed indicating complete utilization of the photons for catalyst activation. Thus, the optimal amount of photocatalyst in DO containing solution is 0.5 – 1.0 g dm^{-3} TiO_2 at the given photon flux.

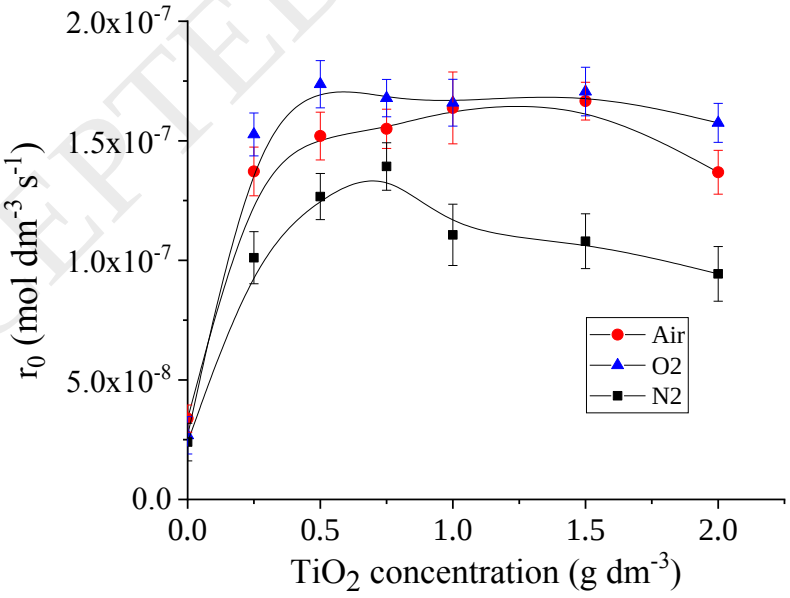


Figure 5. Rate of photocatalytic degradation (r_0) of imidacloprid at 1.0×10^{-4} mol dm^{-3} concentration as a function of TiO_2 concentration in air, O_2 and N_2 saturated solutions.

In our case in DO-free suspension, i.e. in the absence of the effective e_{cb}^- scavenger O_2, imidacloprid transformation with lower rate takes place also and the rate shows maximum between 0.50 and 0.75 g dm^{-3} TiO_2 concentration (Fig. 5). Comparing the emission spectrum of the fluorescent lamp with the absorption spectrum of imidacloprid (Fig. 2), overlapping of the two spectra points out the possibility of direct photolysis. The transformation rate without TiO_2 (2.40×10^{-8}) (Fig. 5) was significantly lower than in the presence of 1.0 mg dm^{-3} TiO_2 (1.1×10^{-7} mol dm^{-3} s^{-1}). When the degradation involves both direct photolysis and photocatalysis, the ratio of the two pathways may vary with TiO_2 concentration, due to the competition for photons between TiO_2 particles and imidacloprid. (The transformation rate of imidacloprid using the fluorescent light source without TiO_2 addition was found to be much smaller (Fig. 6a) than in the solution irradiated with 254 nm light (Fig. 6b). The molar absorbance at 254 nm is much higher than at 300-400 nm (Fig. 2) and probably the quantum yield in 254 nm photolysis is also higher than in 300-400 nm photodecomposition. Moreover, the photon intensities should also be different.)

The strong competition for photons between the TiO_2 particles and imidacloprid can be a reasons of the decrease in the transformation rate over 0.75 mg dm^{-3} TiO_2 in DO free suspension (Fig. 5). Similar concentration dependence of the transformation rate was observed in the photocatalytic degradation of alachlor: the degradation rates increased with TiO_2 concentration, but the reaction was retarded at higher concentrations and finally reached a plateau. In this case the combination of UV photolysis and heterogeneous photocatalysis took place in the suspension [33]. The competition must exist in DO-free and DO containing suspensions, but decrease in the transformation rate over 0.75 mg dm^{-3} TiO_2 was observed only in DO-free ones in our case. DO has no effect on the transformation rate of imidacloprid for direct photolysis (254 nm and 300-400 nm), but strongly enhances that when heterogeneous photocatalysis is applied.

In DO-free solution, at ~1.0 g dm^{-3} TiO_2 concentration, when most of the photons are absorbed by TiO_2 and the contribution of direct photolysis is negligible, the transformation rate becomes constant and it is ~65% of the rate determined in O_2 containing suspension. Similarly to imidacloprid, thiacloprid also transforms in the absence of DO using heterogeneous photocatalysis [34]. Both neonicotinoids react quickly with e_{aq}^-: thiacloprid with a diffusion controlled rate constant (1×10^{10} mol^{-1} dm^3 s^{-1}) [35], while imidacloprid with a relatively high rate constant of 5.1×10^9 mol^{-1} dm^3 s^{-1}. In DO free irradiated suspension,

when photogenerated charges can accumulate on the surface, these neonicotinoids probably behave as e_{cb}^- scavengers instead of O_2, and consequently, undergo degradation. At the same time e_{cb}^- scavenging reduces the extent of e_{cb}^- and h_{vb}^+ recombination and thereby increases the possibility of imidacloprid oxidation via direct charge transfer (h_{vb}^+) and/or via reaction with $^{\bullet}OH$ formed from H_2O/OH^- (Eqs. **2**). Since both imidacloprid concentration (1.0×10^{-4} mol dm^{-3}) and the rate constant of the reaction between imidacloprid and hydrated electron (5.1×10^9 mol^{-1} dm^3 s^{-1}) are much lower than these values for dissolved O_2 (concentration: 1.25×10^{-3} mol dm^{-3}, rate constant: 1.9×10^{10} mol^{-1} dm^3 s^{-1}), the formation rate of each reactive species (including photogenerated charges that escaped recombination, $^{\bullet}OH_{bulk}$ and $^{\bullet}OH_{surf}$) must be significantly lower in DO free suspension than in DO containing ones, and consequently the transformation rate is lower.

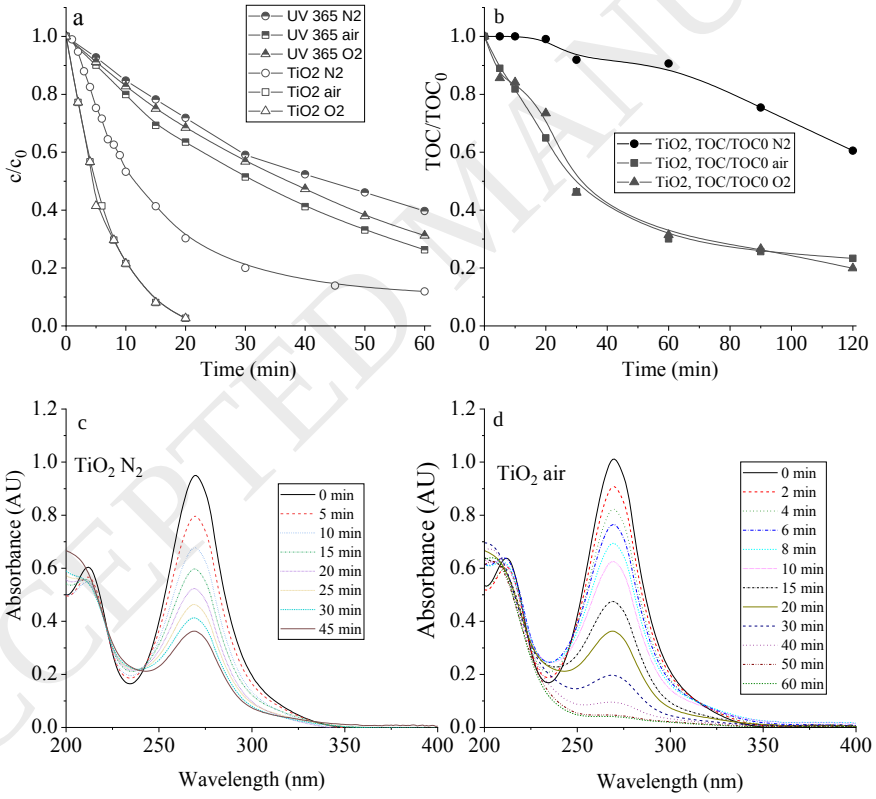


Figure 6. Relative concentration of imidacloprid determined by HPLC-DAD in the presence (O_2, air) and absence (N_2 saturated) of DO, irradiated with the fluorescent lamp without TiO_2 and with TiO_2 (a). TOC measurements during TiO_2 photocatalysis (b). UV absorption spectra of solutions irradiated in the absence (c) and in the presence of DO (d) (treatment times are

indicated in the figures). Initial imidacloprid concentration: 1.0×10^{-4} mol dm^{-3}, TiO_2 concentration: 1.0 g dm^{-3}.

In the absence of DO the TOC content of the samples decreases just slightly during 120 min (Fig. 6b). Since mineralization needs O_2, we assume that the decrease is due to slow degradation to small gaseous fragments which can leave the solution. In air or oxygen bubbled solutions imidacloprid decomposed completely during 20 min and the TOC/TOC_0 values also decreased considerably (~30%). However, the TOC decrease became slower after the complete transformation of imidacloprid, suggesting the presence of intermediate products poorly degradable under the conditions applied.

As the absorption spectra of treated imidacloprid solution show, there is no isosbestic point in the case of aerated suspension. However, at 242 nm an isosbestic point can be observed in oxygen free suspension, reflecting some difference between the transformation way in oxygen containing and oxygen free suspension.

3.2.2. Effects of various scavengers on imidacloprid removal

In heterogeneous photocatalysis, the transformation of organic substances can take place *via* $^{\bullet}OH$ based reactions (with $^{\bullet}OH_{bulk}$ in solution and $^{\bullet}OH_{surf}$ on surface) and/or *via* direct charge transfer on the surface. To unravel the role and contribution of reactive oxygen species and the mechanism of imidacloprid removal in the photocatalytic process, various additives were used: surface modification (NaF), $^{\bullet}OH$ scavengers (methanol and *t*-butanol), $O_2^{\bullet-}$ scavenger (chloroform) and h_{vb}^+ scavengers (EDTA and iodide ion (KI)) in 1:1, 10:1, 50:1 molar ratios of additives to imidacloprid. In Table 1 the degradation rates measured with and without additives are presented together with reaction rate constants of the $^{\bullet}OH$ + additive reactions, taken from the literature [19]. TiO_2 concentration was 1.0 g dm^{-3} in each case. At this concentration most of the photons are absorbed by photocatalyst, and direct photolysis of imidacloprid must be negligible.

Inorganic ions may affect the efficiency of heterogeneous photocatalysis *via* changing the charge and potential of TiO_2 surface and consequently the adsorption properties. F^- has a specific effect in the 2-6 pH range: it can displace the surficial hydroxyl groups (≡Ti-OH) and coordinate surface-bound titanium atoms directly (≡Ti-F) [36,37]. Consequently, the hydrophilicity of the surface decreases due to the presence of F, this phenomenon can strongly effect the adsorption properties. Moreover, this replacement may slightly increase the $^{\bullet}OH$

concentration in the solution *via* hindering the recombination of photogenerated h_{vb}^+ and e_{cb}^-. Both effects are supported by examples from the literature. The degradation rate of phenol, which poorly adsorbs on the TiO_2 surface and transforms mainly *via* $^{\bullet}OH_{bulk}$ based reaction, increases due to the addition of NaF. This was explained by the enhanced direct electron transfer from the aromatic ring to the h_{vb}^+ [36] and by the increased concentration of $^{\bullet}OH_{bulk}$. Furthermore, NaF addition strongly decreased both the adsorbed amount and the transformation rates of phenazopyridin [38] and salicylic acid [39], which were well adsorbed on pristine TiO_2 surface. Similarly to phenol, F^- did not influence measurably the adsorbed amount of imidacloprid. Thus, increase in imidacloprid degradation rate (Table 1) can be explained by the enhanced $^{\bullet}OH_{bulk}$ concentration and/or direct charge transfer between photocatalysts surface and imidacloprid.

The importance of $^{\bullet}OH$ in degradation was reflected by the effect of methanol and *t*-butanol, as widely used $^{\bullet}OH$ scavengers [40]. Inhibition was not observable at 1:1 molar ratio of imidacloprid:methanol or imidacloprid:*t*-butanol in agreement with the much higher rate constant of the imidacloprid + $^{\bullet}OH$ reaction ($(6.97\pm0.54) \times 10^9$ mol^{-1} dm^3 s^{-1}) than those of the *t*-butanol + $^{\bullet}OH$ and methanol + $^{\bullet}OH$ reactions (6.0×10^8 mol^{-1} dm^3 s^{-1} and 9.7×10^8 mol^{-1} dm^3 s^{-1}, respectively [17]). However, by increasing the molar ratio to 1:10, a decrease in the transformation rate unequivocally reveals the dominant role of $^{\bullet}OH$.

Adsorbed DO acts as e_{cb}^- acceptor resulting in the formation of $O_2^{\bullet-}$ (Eq. 3). Chloroform reacts very quickly with $O_2^{\bullet-}$ [41] and can be used to investigate the role of $O_2^{\bullet-}$ [38,42]. Addition of chloroform has no effect even at 1:50 molar ratio, which indicates the negligible role of $O_2^{\bullet-}$ in imidacloprid transformation.

As mentioned before, degradation may also be induced by direct charge transfer. To confirm this possibility, the effect of EDTA was also investigated and its influence was compared to that of methanol and *t*-butanol. EDTA reacts with $^{\bullet}OH$ with lower rate constant (4.0×10^8 mol^{-1} dm^3 s^{-1}) than methanol or *t*-butanol, however, it is quite well adsorbed on the TiO_2 surface and reacts quickly with h_{vb}^+. Beside strong h_{vb}^+ scavenging effect, EDTA may hinder the transformation of target substances *via* competitive adsorption, by retarding the $^{\bullet}OH$ formation rate, because of the competition between EDTA and HO^-/H_2O for reacting with h_{vb}^+ (Eq. 2) and by reacting with $^{\bullet}OH$. Although at 1:1 molar ratio of imidacloprid:methanol/*t*-butanol there was no observable inhibition effect, at the same (1:1) molar ratio EDTA decreased the transformation rate by 65%. Further increase in EDTA concentration (1:50 molar ratio) almost completely inhibited the transformation of imidacloprid. At this molar

ratio (1:50), •OH scavengers brought about less than 60% decrease. The participation of h_{vb}^+ in the transformations was also evaluated by using iodine anion (I^-) scavenger, which effectively reacts with both h_{vb}^+ and •OH [43]. KI had similar effect as EDTA. These facts underline that although the adsorption capacity for imidacloprid is low, beside •OH based reaction, direct charge transfer also takes place in the transformation of imidacloprid.

Table 1. Effect of additives on the transformation rate of imidacloprid. The rate constants were taken from the compilation of Buxton *et al.* [19]. Initial imidacloprid concentration 1.0×10^{-4} mol dm^{-3}, TiO_2 concentration 1.0 g dm^{-3}.

Additive	Molar ratio (imidacloprid:additive)	Rate constant of additives with •OH ($\times 10^8$ mol^{-1} dm^3 s^{-1})	Initial transformation rate ($\times 10^7$ mol dm^{-3} s^{-1})	Relative transformation rate (r/r_0)
pH = 5.5 (ref.)	no additive		1.63	-
pH = 3.0	-		1.06	0.65
pH = 5.5	-		1.70	1.04
pH = 9.0	-		1.83	1.13
NaF	1:1	Not available	2.20	1.35
	1:10		2.20	1.35
	1:50		2.58	1.59
t-Butanol	1:1	6.0	1.77	1.08
	1:10		1.22	0.75
	1:50		0.68	0.42
Methanol	1:1	9.7	1.70	1.04
	1:10		1.18	0.73
	1:50		0.66	0.40
Chloroform	1:1	0.5	1.87	1.15
	1:10		1.77	1.08
	1:50		1.88	1.16
EDTA	1:1	4.0 ($EDTA^{2-}$)	0.56	0.35
	1:10		0.14	0.09
	1:50		0.03	0.02
KI	1:1	110	0.54	0.33
	1:10		0.37	0.23

	1:50	0.02	0.10

The pH has a complex effect on the rate of photocatalytic degradation and its interpretation is a challenging task. pH may change the charge at the surface and thus, the interaction between the semiconductor surface, solvent molecules, substrate, and radicals formed. The point of zero charge (pH_{pzc}) of P25 is between pH 6.30 and 6.60 [44,45]. At pH < pH_{pzc}, the surface of photocatalyst is positively, while at pH > pH_{pzc}, it is negatively charged. Experiments in aqueous TiO_2 suspension were carried out at pH values: 3.0, 6.5 and 9.0, with identical ionic strength adjusted with NaCl (5.0×10^{-3} mol dm^{-3}). The pK_a values for imidacloprid are pK_{a1} = 1.56 and pK_{a2} = 11.12 [46], thus, imidacloprid is in the same protonated form at each pH values (see above). The results obtained in the aqueous suspension of TiO_2 show that, decrease in the pH from 5.5 to 3.0 leads to a decrease in the degradation rate. pH change can influence the generation of $^{\bullet}OH$ via changing the surface charge and it may alter the electrostatic interaction between the charged surface of TiO_2 and imidacloprid, influencing significantly the direct charge transfer [47].

3.3. Decomposition during γ-radiolysis

Fig. 7a shows the imidacloprid concentration determined by HPLC-DAD and the TOC content as a function of absorbed dose, Figs. 7b-7d display the UV absorption spectra of 10^{-4} mol dm^{-3} imidacloprid solution irradiated with γ-rays. In N_2 saturated solutions (reactive intermediates: $^{\bullet}OH$ and e_{aq}^-) and in aerated solutions (reactive intermediates: $^{\bullet}OH$ and the $O_2^{\bullet-}/HO_2^{\bullet}$ pair) at 2 kGy dose imidacloprid completely decomposed. In N_2O saturated solutions (reactive intermediate: $^{\bullet}OH$) some imidacloprid remained at this dose. The intensity of the $\pi \rightarrow \pi^*$ absorption band in the UV spectra with λ_{max} at 270 nm decreases steadily with the absorbed dose (Figs. 7b-7d). The UV spectra reflect very similar results to those obtained by the HPLC-DAD method.

The yield of imidacloprid decay, based on the first concentration data points at low dose, is calculated to be ~0.14 μmol J^{-1} both in N_2 and air saturated solutions, while it is ~0.1 μmol J^{-1} in solution saturated with N_2O. These yields are much smaller than the $^{\bullet}OH$ yields: 0.28, 0.28 and 0.56 μmol J^{-1}, respectively. In N_2 saturated solution e_{aq}^-, under aerated conditions the $O_2^{\bullet-}/HO_2^{\bullet}$ pair may slightly contribute to imidacloprid degradation.

Formerly we discussed the possibility of HCH radical formation in $^{\bullet}OH$ reaction. As it was mentioned, these radicals are expected to transform to phenol type stable products [29]. The

UV absorption spectra of phenol type derivatives are usually shifted by 20-30 nm to longer wavelengths, compared to the initial compounds. When aromatic OH derivatives form, new peaks or shoulders appear on the long wavelength side of the main peak. This was not observed here, which is also in disagreement with a higher contribution of aromatic ring hydroxylation. Hydroxylated pyridine ring containing products forming in the •OH + imidacloprid reactions were not described in the literature [26,28] either. •OH addition to the aromatic ring with low yield was suggested in the case of thiacloprid [22,33].

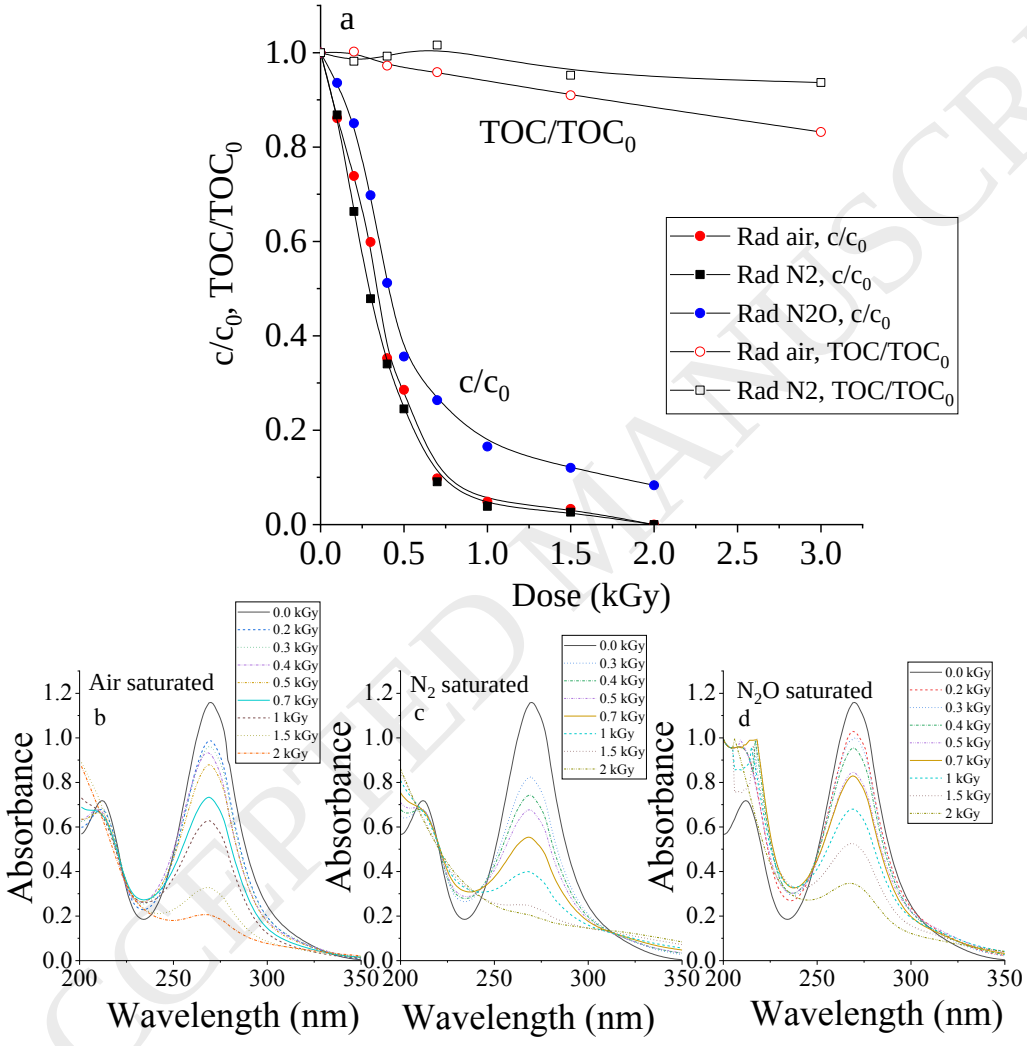


Figure 7. Degradation of imidacloprid determined by HPLC-DAD and TOC measured during γ-radiolysis in the presence and absence of DO (a). UV absorption spectra of solutions irradiated in the presence of air (b), N_2 (c) and N_2O (d). Initial imidacloprid concentration 1.0 × 10^{-4} mol dm^{-3}.

In the samples irradiated in N_2 saturated solutions practically no decrease in the TOC value was observed. In air saturated solution at ~2 kGy dose, when the imidacloprid molecules disappeared from the solution ~10% decrease in TOC was found.

3.4. UV- and UV/VUV photolysis

The UV absorption spectra of the imidacloprid solutions were taken (Fig. 8b and 8c), products were separated by HPLC-DAD to determine the degradation rate of imidacloprid (Fig. 8a) and TOC measurements were performed to follow the transformation of the organic content during the treatments. As the figures show, efficient imidacloprid removal was experienced under all conditions. The UV/VUV process was somewhat more effective than the UV treatment. In the UV/VUV process, under the conditions used, 10 min. were sufficient for practically complete imidacloprid removal (Fig. 8a). During this time in UV irradiation the concentration of imidacloprid decreased by about 85%. However, the further decrease was much slower. The degradation rate was not much dependent on the DO. The UV absorption spectra of solutions irradiated in the presence of DO (Figs. 8b and 8c) were practically identical to the spectra taken in solutions irradiated in the absence of DO (not shown). In the spectra of UV treated solutions, both in the presence and absence of DO, after 8 min isosbestic points appeared at 248 and 278 nm.

In case of the combined UV/VUV photolysis (Fig. 8a) efficient mineralization could be achieved both in oxygenated and non-oxygenated solutions. The TOC content decreased steeply with treatment time. It was 40% at 10 min and in the first 50-60 min of treatment reached ~80% mineralization. In the next 60 min the mineralization increased by only 5%, suggesting the presence of very stable degradation products, resisting even the primary water radicals generated by the VUV light.

Although DO does not contribute to the direct degradation of the target compound, a significant effect could be observed on the mineralization of the solution during UV photolysis (Fig. 8a). In DO-free conditions, the TOC content decreased by 10% in the first 10 min, and then the rate of decrease slowed down, reaching only ~13% after 120 min. In the presence of DO the decrease of the TOC content was 15% at 20 min and at 30 min it reached ~35% mineralization. In the next 90 min the mineralization rate slowed down, reaching ~50% of mineralization for 120 min treatment. The above results show that some of the formed intermediate products can have very low ε_{254}, and/or very low quantum yield of degradation, therefore, they are not degradable by UV photolysis alone. The radical degradation (that is

effective in VUV photolysis) contributes significantly to the mineralization degree of the formed compounds.

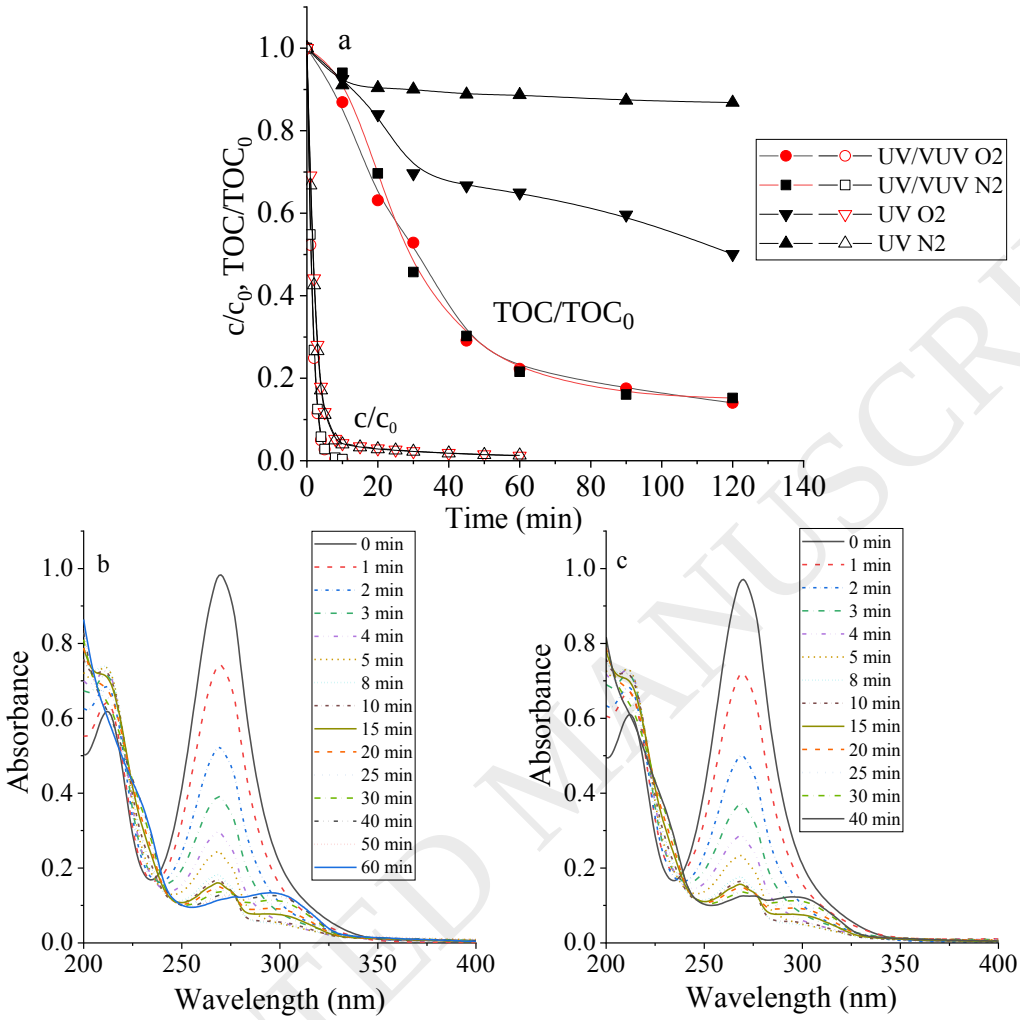


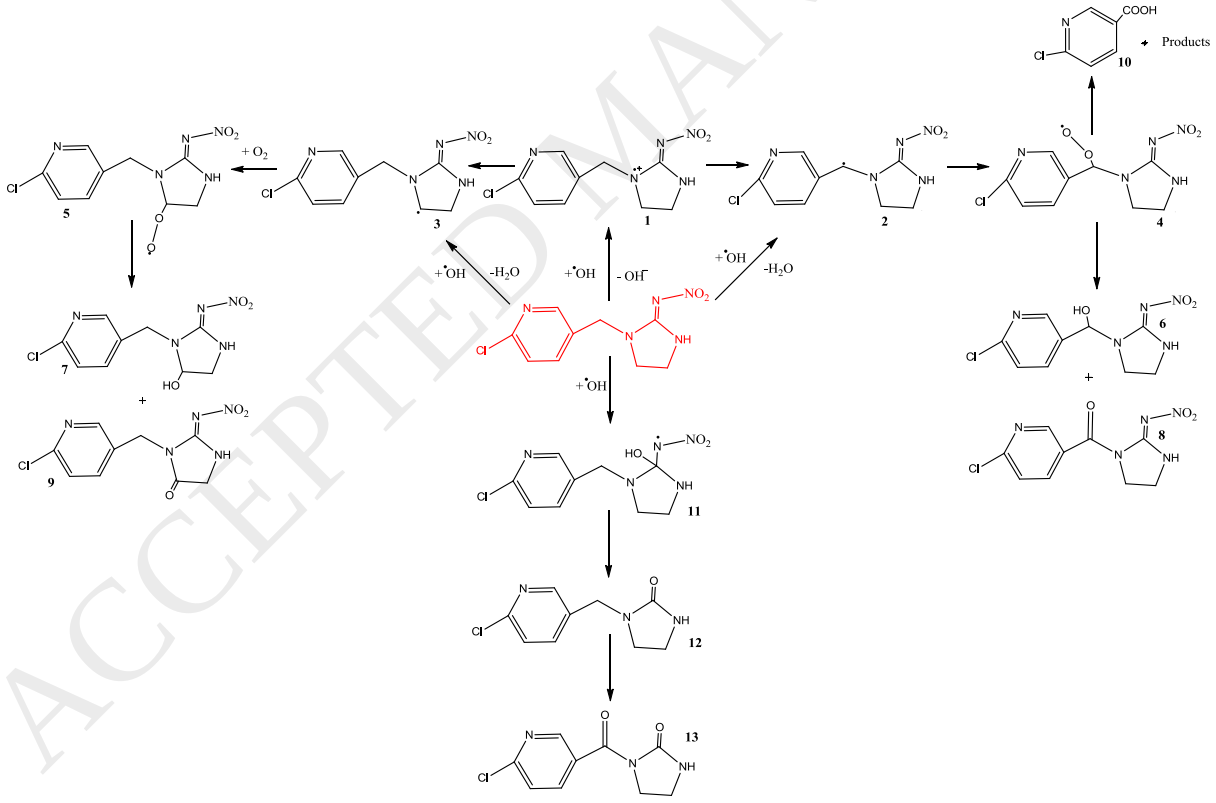
Figure 8. Degradation of imidacloprid determined by HPLC-DAD (open symbols) and by TOC measurements (closed symbols) during UV/VUV- and UV photolysis in the presence and absence of DO (a). UV absorption spectra of UV/VUV- (b) and UV (c) irradiated solutions with DO. Initial imidacloprid concentration: 1.0×10^{-4} mol dm^{-3}.

3.5. Product analysis and degradation mechanism

The stable products were analysed by HPLC separation and DAD detection at 270 nm, and MS detection for product identification. Detailed product analysis was performed only on samples treated in the presence of DO. Our analysis, in agreement with literature results, leads to two main conclusions. Independently of the method used, with slight variation, in all cases the same products were observed. This is surprising, because in UV photolysis the directly

excited solute molecules, while in radiolysis the one-electron oxidants/reductants (free radicals), induce the chemical changes. In the UV/VUV process and in TiO_2 photocatalysis the radical chemistry plays also an important role. In UV photolysis formation of α-aminoalkyl radicals is highly favoured [48], just as in the •OH based reactions (see pulse radiolysis). Therefore, the similar product spectrum can be due to the dominance of the same intermediates. The other conclusion was that during our experiments the reaction involved only the imidazolidine moiety of the molecule, while the 6-chloropyridine moiety remained unchanged. No products were observed with modified 6-chloropyridine structure.

The possible formation of isomers makes the evaluation of product formation difficult. E.g., hydroxylation may take place at any of the three CH_2 units of the molecule. These hydroxylated molecules are expected to be separated by the applied HPLC method. We must mention that in most cases only one isomer was detected on the chromatograms. The stable products in the case of such complex molecule may undergo several rearrangement and hydrolysis processes [49], these reactions also make it difficult to establish the reaction mechanism.



Scheme 1. Degradation mechanism suggested (1. imidacloprid radical cation, 2. and 3. benzyl/α-aminoalkyl radical and α-aminoalkyl radical, 4. and 5. peroxy radicals, 6. and 7. hydroxy-imidacloprids, 8. and 9. oxo-imidacloprids, 10. 6-chloronicotinic acid, 11. N-centred

aminyl type radical, 12. 1-(6-chloro-3pyridilmethyl)imidazolidin-2-one, 13. oxidized urea type product (several isomers)).

A tentative reaction mechanism based on $^{\bullet}$OH reactions, which explains the formation of main products, is shown in Scheme 1. The analysis of the transient spectrum obtained in our pulse radiolysis experiments suggests that the main reactive intermediates are α-aminoalkyl radicals. The two most probable variations are indicated in Scheme 1 by **2** and **3**. These intermediates may form in H-atom abstraction from the CH_2 units, or in deprotonation reaction of radical cation **1**. The carbon centred radicals, **2** and **3** are expected to react quickly with DO and transform to peroxy radicals, **4** and **5**. The reactions of the peroxy radical may give hydroxylated (**6** and **7**) and carbonylated (**8** and **9**) products. Yin *et al.* [14] suggested $O_2^{\bullet-}$ elimination from the peroxy radical **4**, and hydrolysis of the remaining organic molecule with bond breaking between the CH_2 bridge and the imidazolidine ring. We identified 6-chloronicotinic acid (**10**) as a product of this bond breakage. In UV reaction formation of 6-chloronicotinic alcohol [13], and in TiO_2 and in H_2O_2 activation reactions that of 6-chloronicotinic aldehyde have also been reported in the literature [5,6,26].
$^{\bullet}$OH can also be added to the double bond of the nitroimino part of imidacloprid. In the reaction radical **11** might form. Due to the strong electron-withdrawing nitro group the radical attack is expected at the carbon atom and the unpaired electron is proposed to be localized on the nitrogen. Thus, aminyl type radical forms, which usually does not show absorption in the UV range and therefore cannot be directly identified from the transient spectra. We assume that the degradation/hydrolysis of this radical gives the urea type product **12**. In further oxidations of products **8**, **9** and **12** isomers of compounds with two carbonyl groups may form (one possibility is **13**).

3.6. Comparison of the AOP techniques

All the methods tested can degrade imidacloprid molecules. These molecules decompose in systems where aggressive $^{\bullet}$OH can initiate the reaction, like in TiO_2 photocatalysis, in radiolysis and also in UV/VUV photolysis. Direct reaction takes place in UV photolysis. However, as we have shown, the photons (300-400 nm) used to excite TiO_2 also degrade imidacloprid, although, the photocatalytic process is dominant in degradation.
In most cases the mineralization and the disappearance of the starting molecules occurs parallel. However, the extents of mineralization at the point when the initial molecules

disappear from the solution are highly different. In oxygenated solutions the highest decreases in TOC values, 30-40% were found in UV/VUV and TiO_2/O_2 systems. In radiolysis and UV photolytic systems these values were 10-15%. In the absence of oxygen the mineralization was usually slower than in its presence.

Although all the methods can be used in imidacloprid degradation, there are great differences in the efficiencies. This is especially true for the electric energy utilization (E_{EO}) needed to decrease the imidacloprid concentration by an order of magnitude (from 10^{-4} mol dm^{-3} to 10^{-5} mol dm^{-3}, Fig. 9). These values were calculated based on the energy demand of the lamps used in UV, UV/VUV and photocatalysis techniques. In radiolysis the absorbed radiation energy (kGy) was the basis of the calculation. However, in practical applications for water purification instead of gamma source applied in our stable product analysis, electron accelerators are used. In the electron accelerators used for wastewater treatment about 75% of the electric energy is converted to the energy of accelerated electrons [50]. Therefore, the value calculated for radiolysis using Equ. 15, was corrected by dividing it with 0.75.

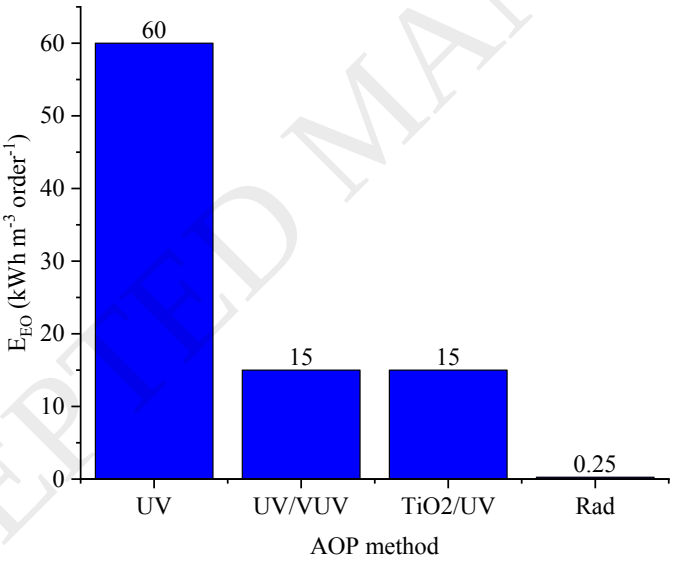


Figure 9. E_{EO} values for the decrease of imidacloprid concentration from 10^{-4} to 10^{-5} mol dm^{-3} using the methods studied in DO containing solutions. TiO_2 concentration: 1.0 g dm^{-3}.

As Fig. 9 shows the UV technique has the highest energy consumption. At the same time this technique is the less efficient in the elimination of the degradation products. The E_{EO} values for UV/VUV and photocatalysis are similar and much lower than that for UV. In the elimination of the degradation products photocatalysis was the most efficient. Similarly to our previous

experiences [35] the energy demand of radiolysis is smaller by c.a. two orger of magnitude as those of the other methods.

4. Conclusions

Based on pulse radiolysis experiments α-aminoalkyl radicals were suggested as main intermediates in •OH induced reactions. The structures of the stable products at the beginning of the treatments are practically the same in TiO_2 photocatalysis, UV/VUV and UV photolysis and γ-radiolysis. It is assumed that α-aminoalkyl radicals play important role in all these processes.

Dissolved oxygen has usually not much effect on the initial degradation rate of imidacloprid molecules in UV/VUV and UV photolysis and in radiolysis, although some enhancement is observed. In the case of heterogeneous photocatalysis the electron acceptor effect of O_2 is important to prevent charge recombination. However, in this case imidacloprid transformed without DO, which was explained by the importance of direct charge transfer.

Based on the degradation and mineralization results of the imidacloprid transformation, photocatalysis, UV/VUV photolysis and radiolysis seem to be successful methods for water purification purposes. Regarding economic considerations (E_{EO}) radiolysis seems to be the most suitable technique.

Acknowledgment

This Special Issue is dedicated to honour the retirement of Prof. César Pulgarin at the Swiss Federal Institute of Technology (EPFL, Switzerland), a key figure in the area of Catalytic Advanced Oxidation Processes. Our team had the privilege to work with Professor Pulgarin in a cooperation, in the frame of a Swiss-Hungarian project. The project was initiated by him, lasted 5 years and resulted in, beside several publications, a design of a complex plant, treating process wastewaters of the pharmaceutical industry, attached to a municipal wastewater treatment plant of 100.000 m^3/day capacity.

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Declarations of interest: none

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